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(54) PROCESS FOR PRODUCTION OF ATTRITION RESISTANT
 ANTIMONY OXIDE CONTAINING FLUIDIZED BED
 CATALYST HAVING CONTROLLED PARTICLE SIZE
 DISTRIBUTION

(71) We, NITTO CHEMICAL INDUSTRY CO., LTD., a Japanese Company of No. 5-1, Marunouchi 1-chome, Chiyoda-ku, Tokyo, Japan, do hereby declare this invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This present invention relates to a process for production of a solid catalyst containing antimony oxide as one of the effective components and suitable for use in fluidized bed reactions. More particularly, it is concerned with a process for production of a fluidized bed solid catalyst containing attrition-resistant antimony oxide which does not contain extremely fine particles nor coarse particles unsuitable for practical use and whose particle diameter is controlled.

Antimony oxide-containing catalysts are useful for ammonoxidation of olefins to the corresponding unsaturated nitriles, oxidation of olefins to the corresponding aldehydes, and oxidative dehydrogenation of olefins to the corresponding diolefines. These catalysts are described, for example, in U.S. Patent Nos. 3,657,155; 3,686,138; 3,716,496 and 3,988,359. The above described reactions can be effected in either a fixed bed or a fluidized bed, but they are generally carried out in a fluidized bed with which it is easy to remove the reaction heat since the heat of reaction thereof is high. In this fluidized bed reaction, it is important of course, for the activity and strength of the catalyst to be high for the reaction to proceed effectively by keeping the catalyst particles in a well fluidized state. It is also well known that a particle size distribution is very important. The particle diameter of the catalysts used in this fluidized bed reaction

is generally not more than 500 μ and the average particle diameter is generally in a range of about 40 μ to 200 μ .

With regard to a process for production of an antimony oxide-containing fluidized bed catalyst, a method has been proposed comprising preparing a slurry containing an antimony compound, a polyvalent metal compound and a silica sol as essential components, adjusting the pH of the slurry, heat-treating the slurry, subjecting the slurry so-treated to a spray-drying operation to form spherical particles, and calcining the resulting particles, as described in U.S. Patent Nos. 3,657,155 and 3,686,138. In this process, a catalyst having the desired particle size distribution is produced by controlling the spray-drying conditions. However, with such an operation, it is quite difficult to produce a catalyst having the desired particle size distribution in that unnecessarily small catalyst particles are more or less inevitably produced. In a fluidized bed reaction, these small catalyst particles cause the problems in that they are quickly lost during the reaction, resulting in a reduction in the yield of the required product, in an increase in catalyst unit cost and in an increase in the amount of waste solids, the latter resulting in pollution problems. On the other hand, if the above described spray-drying conditions are controlled to produce catalyst particles having larger particle diameters so that the above described problems are eliminated, catalyst particles having a particle size distribution in which coarse particles are predominant are produced. This causes fluidization problems which reduce the effect of the catalyst.

The problem arises in the fluidized bed reaction that even though catalyst particles having a suitable size distribution are

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employed, the catalyst particles of small diameter are inevitably scattered and lost, and thus the proper particle size distribution is destroyed and the catalyst particles of greater diameter become predominant. In this case, it is necessary to produce make-up, small diameter catalyst particles so that the proper particle size distribution is maintained. In producing catalysts with appropriate particle diameters for make-up, however, it is quite difficult solely by controlling the above described spray-drying conditions, to obtain a catalyst of the desired particle size distribution.

Under these circumstances, the catalyst particles of relatively small diameter have inevitably been produced and used as a make-up catalyst, and thus it has been considered inevitable that the amount of the particles to be scattered and lost will increase during the use thereof.

A process for production of an antimony oxide-containing fluidized bed catalyst has also been proposed as described in Japanese Patent Application (OPI) No 40288/1974, for useful utilisation of coarse catalyst particles formed during use of the catalyst. In accordance with this process, the coarse catalyst is pulverized to particles of a diameter of 20 μ or less, and the pulverised catalyst is incorporated into the slurry at an appropriate step prior to the spray-drying according to the method disclosed in U.S. Patent No. 3,657,155 so that the pulverized catalyst constitutes not more than 50% by weight of the total catalyst weight.

This method of producing catalysts can be utilised as a method of producing catalysts for controlling the particle diameter. Thus, it is possible to produce a catalyst of the desired particle size distribution by removing extremely fine particles and/or coarse particles unsuitable for practical use. However, since the catalyst removed has been calcined at elevated temperatures and has a high strength, the pulverization thereof requires a great deal of energy. In addition, at the time of the spray-drying of the slurry with the catalyst incorporated therein, parts of the equipment such as a slurry pump and nozzles are subjected to a high degree of abrasion and frequent change of parts is needed. Furthermore, in this case, the amount of the pulverized catalyst which can be incorporated is limited, i.e. if the pulverized catalyst is added in an amount above 50% by weight, the strength of the final catalyst markedly decreases and thus the final catalyst becomes unsuitable for practical use.

An object of the present invention is to obviate or mitigate the above described problems.

According to the present invention, there

is provided a process for producing an attrition-resistant, antimony oxide-containing fluidized bed catalyst having a controlled particle size distribution, said process comprising (a) preparing a slurry containing at least one antimony compound, one or more polyvalent metal or metalloid compounds and a silica sol as essential components and in addition, if necessary, ferric ions and nitrate ions, (b) adjusting the pH of the resulting slurry to not more than 7 and heating the slurry for at least 20 minutes, at a temperature of 40°C to 150°C while keeping the mixture in a slurried state to form a catalyst slurry containing pentavalent antimony, (c) spray-drying the slurry thus obtained to form substantially spherical particles, (d) separating extremely fine particles and/or coarse particles unsuitable for practical use from the above spherical particles and returning the separated extremely fine and/or coarse particles to the slurry prior to the spray-drying in step (c) either untreated or after pulverization thereof, and (e) calcining the particles from which the extremely fine particles and/or coarse particles unsuitable for practical use have been removed at a temperature of from 400°C to 1100°C.

The process of the present invention is preferably applicable particularly to Sb-Fe based catalysts which contain or which do not contain a small amount of promoter. In preferred catalysts, the atomic ratio of the metal or metalloid in the polyvalent metal or metalloid compound to the antimony in the antimony compound is in the range of from 1:10 to 5:1, and the highest activity is obtained in the range of from 1:5 to 1:1.

Antimony compounds which can be used in the present invention include a nitric acid oxidized metallic antimony (i.e. the product of oxidation of metallic antimony with nitric acid), basic antimony nitrate, antimony trioxide, antimony pentoxide, antimonic acid, antimony trichloride, antimony pentachloride, a hydrolysis product of antimony trichloride, the oxidized product of antimony trioxide with hydrogen peroxide, and antimony pentoxide sol. It is preferred, however, that the chlorides are used after the removal of excess chloride ion by hydrolysis. These compounds are preferably present as a fine dispersion in an aqueous medium, more preferably in a colloidal state or in a state similar to that of a solution. Other oxidants such as hydrogen peroxide or potassium permanganate can also be used.

Where a trivalent antimony compound is used in the formation of the slurry, in one method (i), the trivalent compound is oxidized in the slurry heating step hereinafter described. For this reason, it is

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- necessary for ferric ions and nitrate ions to be present in the slurry for forming the catalyst. Where ferric nitrate is used as a polyvalent metal compound, the above requirement is naturally satisfied. However, where other compounds are used, they must be used in combination with those compounds capable of releasing ferric ions and/or nitrate ions.
- With regard to the amount of the ferric ion in the slurry, it is at least 1 g ion per 100 g atom of antimony, preferably 5 to 500 g ion. With regard to the amount of the nitrate ion in the slurry, it is 1 to 2000 g ion equivalent per 100 g atom of antimony, preferably from 50 to 2000 g ion equivalent.
- As suitable iron ion sources, those compounds capable of releasing ferric ions in the slurry can be used, and soluble ferric salts such as ferric nitrate and ferric hydroxide can be used. As nitrate ion sources, those corresponding to the ions present in the starting materials of the catalyst such as nitric acid oxidized antimony and nitrates of polyvalent metals can be utilized. In addition, nitric acid can be used as a nitrate ion source.
- In another method (ii), trivalent antimony can be oxidized prior to the heat processing of the slurry or at the time of processing using oxidizing agents such as hydrogen peroxide or potassium permanganate.
- The one or more polyvalent metal or metalloid compounds which can be used in the process of the present invention is or are compounds selected from iron, cobalt, nickel, tin, uranium, chromium, copper, manganese, titanium, vanadium, molybdenum, tungsten, tellurium, bismuth, thorium, cerium, magnesium, zinc, aluminium and zirconium. These polyvalent metal or metalloid compounds can be used individually or in combination with each other.
- The nitrate salts of iron, cobalt, nickel, uranium, chromium, copper, manganese, bismuth, thorium, magnesium, zinc, aluminium and zirconium can be conveniently used as starting materials for these components. As the starting material for the vanadium component, a water-soluble compound such as ammonium metavanadate or vanadyl oxalate can be conveniently used. As the starting materials for the molybdenum and tungsten components, ammonium paramolybdate, ammonium paratungstate and the other water-soluble compounds can be conveniently used.
- Suitable starting materials for tellurium include the oxides thereof, such as tellurium dioxide and nitric acid oxidized tellurium (i.e. the oxidation product of tellurium with nitric acid), tellurous acid and telluric acid. As the starting materials for the titanium and tin components, the chlorides thereof can be used.
- As the silica sol, a suitable one can be selected from commercially available silica sols. The concentration of the silica sol may be used in a range of from 5 to 90% by weight as silicon dioxide content, and generally in a range of from 10% by weight to 50% by weight. The amount of the silica sol to be used corresponds to 10 to 90 parts by weight, as silicon dioxide, per 100 parts by weight of the final catalyst.
- The particles separated in step (d) may be introduced into the slurry at the time when ferric ions and nitrate ions are introduced into the slurry when the antimony compound is a trivalent antimony compound. At this time, the slurry concentration is preferably in the range of from 0.5 to 50% by weight, calculated as the oxide of the element forming the catalyst. While the order of adding the catalyst components is not critical, those compounds in a solution state, a colloidal state and a particle dispersion state in which precipitation easily takes place, are added in this order from the point of view of ease of operation and dispersion uniformity of the components.
- Then the pH of the slurry is adjusted to not more than 7 preferably to a pH in the range of from 1 to 4. In adjusting the pH, the slurry is stirred well so that a localized increase in pH can be prevented. Volatile acids or volatile bases can be used as pH adjusting agents. Examples of acids which can be used include nitric acid, various kinds of organic acids such as formic acids, oxalic acid, citric acid and tartaric acid, carbon dioxide gas or aqueous carbonic acid solution. Of these compounds, nitric acid is particularly preferred. Aqueous ammonia, organic amines, such as methylamine, ethylamine and aniline, pyridines and quinolines can be used as bases. Of these compounds, aqueous ammonia is most preferred.
- The slurry prepared as hereinabove described is then preferably heated at a temperature of from 80 to 100°C for at least 20 minutes and for preferably 1 to 12 hours. By this processing, complicated physical and chemical changes take place in the slurry so that attrition resistance is provided to the catalyst. During the period of this heating processing, all or at least one of the following phenomena are observed:— an increase in viscosity of the slurry, a variation in pH and in colour tone, a pulverization in the antimony compound particles, a change in the antimony atomic valence of one portion of the antimony compound ($Sb^{III} \rightarrow Sb^V$), a quantitative change in free trivalent iron, a qualitative and quantitative change

- in silica particles in the sol state and a formation of nitrous acid. These phenomena suggest that the various types of catalyst components present in the slurry are being subjected to complicated chemical changes.
- The above heating processing may be carried out either using a system in which the slurry is concentrated in an open apparatus, or a system in which the water evaporated from the slurry is recycled in a closed system. In general, where a dilute slurry is subjected to heating processing, the former system is advantageously employed, whereas where a concentrated slurry is subjected to heating processing, the latter system is advantageously employed.
- In this heating processing, it is important for the processing to be carried out while keeping the mixture in a slurry state, and in any case, evaporation to dryness should be avoided. The preparation and heating processing of the slurry are preferably carried out with uniform agitation. Thus, the use of a means of agitation such as stirrer is recommended. In the present invention, those particles to be admixed can be mixed with the slurry subjected to the heating processing.
- The slurry containing pentavalent antimony which has been subjected to the heating processing is then spray dried to form substantially spherical particles. The spray drying conditions are not critical and known techniques and conditions can be employed as they are. For example, the pressure nozzle type, the two fluid nozzle type or the rotary disc type of spray dryer can be used. The slurry concentration to be charged to the spray dryer preferably ranges from 10 to 50% by weight, calculated as the oxides of the elements constituting the catalyst.
- The temperature of the spray drying is not critical. It is preferred from the point of view of convenience of operation for the slurry which has been subjected to the heating processing or the slurry to which a pulverized catalyst has been added, to be subjected to spray drying operation immediately and without any additional treatment. However, this is not essential. The slurry may be subjected to spray drying after a lapse of a long period of time if such is appropriate for operational reasons, and after adjusting the slurry concentration, the slurry may be subjected to spray drying.
- While the temperature at which the spray drying is effected is not critical, it is preferred for the temperature of the hot air used for the drying to be at a temperature of from 200 to 500°C, more preferably from 300 to 400°C, at the inlet of the apparatus and at a temperature of from 100 to 300°C, more preferably from 100 to 200°C, at the outlet of the apparatus. The atmosphere into which the spray drying is effected is not critical, but it is preferably effected in a reducing atmosphere. For economic reasons, combustion gases containing an excess of air are advantageously used.
- By this spray drying, spherical particles whose particle diameters usually fall in a range of from 5 to 200 μ, are formed. The extremely fine particles and/or coarse particles are separated from these particles.
- The particle diameter of the extremely fine particles and/or coarse particles to be separated out varies with the fluidized reaction apparatus and reaction conditions, and also with the particle density of the catalyst. Therefore, taking into account the physical properties of the catalyst and the conditions under which the catalyst is to be used, the diameter of the particles to be separated should be determined. Generally speaking, however, the extremely fine particles to be separated have a diameter of not more than 10 to 30 μ and the coarse particles to be separated have a diameter of not less than 60 to 200 μ depending upon the circumstances. Also, those cakes formed at the time of spray drying (those attached to the inner surface of the spray drying apparatus) can be considered to be coarse particles. With regard to the spherical particles from which the extremely fine particles and/or coarse particles have been separated, it is preferred for those particles having diameter of not more than 20 μ to constitute not more than 5% by weight of the total particles and those particles having a diameter of not less than 20 μ to constitute not more than 15% by weight of the total weight of the particles.
- Separation of the extremely fine particles can be effected using a cyclone separator attached to the spray drying apparatus, and where the separation must be carried out strictly, the separation can be conducted by installing a classification apparatus. In particular, where the catalyst for use as make-up as described above are produced, a catalyst having a narrow distribution of relatively small particles and containing neither extremely fine particles nor coarse particles is preferred, and in this case, the use of the classification apparatus is preferred. In such a classification operation, the spray dried particles are less likely to be subjected to fracture and abrasion than in a cyclone separator.
- On the other hand, the extremely fine particles and/or coarse particles separated as described above are pulverized using e.g. a known grinder such as a colloid mill, a ball mill, or a vibration mill. Pulverization to a high extent is especially preferred. At this time, either water may be added to the particles or the slurry prior to the spray.

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in silica particles in the sol state and a formation of nitrous acid. These phenomena suggest that the various types of catalyst components present in the slurry are being subjected to complicated chemical changes.

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The above heating processing may be carried out either using a system in which the slurry is concentrated in an open apparatus, or a system in which the water evaporated from the slurry is recycled in a closed system. In general, where a dilute slurry is subjected to heating processing, the former system is advantageously employed, whereas where a concentrated slurry is subjected to heating processing, the latter system is advantageously employed.

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In this heating processing, it is important for the processing to be carried out while keeping the mixture in a slurry state, and in any case, evaporation to dryness should be avoided. The preparation and heating processing of the slurry are preferably carried out with uniform agitation. Thus, the use of a means of agitation such as stirrer is recommended. In the present invention, those particles to be admixed can be mixed with the slurry subjected to the heating processing.

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The slurry containing pentavalent antimony which has been subjected to the heating processing is then spray dried to form substantially spherical particles. The spray drying conditions are not critical and known techniques and conditions can be employed as they are. For example, the pressure nozzle type, the two fluid nozzle type or the rotary disc type of spray dryer can be used. The slurry concentration to be charged to the spray dryer preferably ranges from 10 to 50% by weight, calculated as the oxides of the elements constituting the catalyst.

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The temperature of the spray drying is not critical. It is preferred from the point of view of convenience of operation for the slurry which has been subjected to the heating processing or the slurry to which a pulverized catalyst has been added, to be subjected to spray drying operation immediately and without any additional treatment. However, this is not essential. The slurry may be subjected to spray drying after a lapse of a long period of time if such is appropriate for operational reasons, and after adjusting the slurry concentration, the slurry may be subjected to spray drying.

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While the temperature at which the spray drying is effected is not critical, it is preferred for the temperature of the hot air used for the drying to be at a temperature of from 200 to 500°C, more preferably from 300 to 400°C, at the inlet of the apparatus and at a temperature of from 100 to 300°C, more preferably from 100 to 200°C, at the outlet of the apparatus. The atmosphere into which the spray drying is effected is not critical, but it is preferably effected in a reducing atmosphere. For economic reasons, combustion gases containing an excess of air are advantageously used.

By this spray drying, spherical particles whose particle diameters usually fall in a range of from 5 to 200 μ, are formed. The extremely fine particles and/or coarse particles are separated from these particles.

The particle diameter of the extremely fine particles and/or coarse particles to be separated out varies with the fluidized reaction apparatus and reaction conditions, and also with the particle density of the catalyst. Therefore, taking into account the physical properties of the catalyst and the conditions under which the catalyst is to be used, the diameter of the particles to be separated should be determined. Generally speaking, however, the extremely fine particles to be separated have a diameter of not more than 10 to 30 μ and the coarse particles to be separated have a diameter of not less than 60 to 200 μ depending upon the circumstances. Also, those cakes formed at the time of spray drying (those attached to the inner surface of the spray drying apparatus) can be considered to be coarse particles. With regard to the spherical particles from which the extremely fine particles and/or coarse particles have been separated, it is preferred for those particles having diameter of not more than 20 μ to constitute not more than 5% by weight of the total particles and those particles having a diameter of not less than 20 μ to constitute not more than 15% by weight of the total weight of the particles.

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Separation of the extremely fine particles can be effected using a cyclone separator attached to the spray drying apparatus, and where the separation must be carried out strictly, the separation can be conducted by installing a classification apparatus. In particular, where the catalyst for use as make-up as described above are produced, a catalyst having a narrow distribution of relatively small particles and containing neither extremely fine particles nor coarse particles is preferred, and in this case, the use of the classification apparatus is preferred. In such a classification operation, the spray dried particles are less likely to be subjected to fracture and abrasion than in a cyclone separator.

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On the other hand, the extremely fine particles and/or coarse particles separated as described above are pulverized using e.g. a known grinder such as a colloid mill, a ball mill, or a vibration mill. Pulverization to a high extent is especially preferred. At this time, either water may be added to the particles or the slurry prior to the spray.

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5 drying may be mixed. On account of the insufficient strength of the particles, the pulverization of the particles can be effected relatively easily and most of the particles can be pulverized to a size of several microns or less in a short time by wet pulverization. Since the large particles contained in the slurry deteriorate the condition of the finished catalyst, it is preferred for most of the particles to be pulverized to not more than 10μ . Depending upon the composition of the catalyst, and spray drying conditions, the particles can be sometimes pulverized only by mixing with water without applying any pulverization processing.

10 The thus obtained extremely fine particles or pulverized particles are mixed with the slurry prior to the spray drying thereof as described above. Incorporation of the particles into the slurry prior to the spray drying can be effected during the step of preparing the slurry such as on mixing of the starting materials for the catalyst, or 15 during the adjustment of the pH. Alternatively, the particles can be incorporated into the slurry after the heating processing. Thus, the step at which the particles are incorporated is determined 20 solely by ease of operation to prepare the catalyst. It is most convenient for operation for the particles to be incorporated into the slurry after the heating processing, but no marked change occurs in the characteristics 25 of the finished catalyst regardless of when the particles are added. This mixing can be effected by the use of usual stirring apparatus or homogenizer.

30 The slurry with the above particles mixed therewith as described above, which is prior to the spray drying, is subjected to a spray drying operation to form substantially spherical particles and to separate the extremely fine particles and/or coarse 35 particles.

35 It is possible for the above described extremely fine particles and/or coarse particles not to be mixed with the slurry prior to the spray drying, but for an aqueous slurry of the particles alone to be prepared 40 and subjected to the spray drying to form spherical particles.

45 It is preferred for spherical particles from which extremely fine particles and/or coarse particles have been removed to be heated at 200 to 600°C for 0.5 to 20 hours to remove water, salts and other volatile components. The spherical particles are then subjected to a calcination at a temperature ranging from 50 400 $^{\circ}\text{C}$ to 1100 $^{\circ}\text{C}$ preferably for 0.5 to 50 hours to prepare the catalyst.

55 The manner in which these two heating steps are effected is not critical, and they can be effected in a furnace such as a box-type furnace, a tunnel furnace, a rotary

furnace or a fluidized bed furnace. As a method of heating, gas heating or electric heating can be employed.

60 In accordance with the method of the present invention, those extremely fine particles and/or coarse particles separated from the spherical particles, which have been obtained by the spray drying of the slurry, are re-cycled, thereby increasing the production efficiency of the catalyst, which is quite advantageous from an economic standpoint. Since the extremely fine and/or coarse particles are not calcined and have a low strength, where a pulverization thereof is required, the pulverization can be easily carried out. Furthermore, in the spray drying of the slurry containing these particles, the spherical particles can be produced without causing the problem of abrasion of the apparatus. In addition, the thus produced catalyst whose diameter has been controlled is a practical catalyst having a high strength and a sufficient activity.

65 Since the finished catalyst does not contain any extremely fine particles, the loss of the catalyst through the reaction is small and the catalyst consumption is decreased. Therefore, the formation of catalyst waste decreases.

70 Moreover, where the fine particle portion of the catalyst is scattered and lost during the reaction and the particle size distribution moves to a larger particle diameter, resulting in a deterioration of the fluidized state and a reduction in contacting efficiency, catalyst having the desired particle diameter, i.e. containing hardly any extremely fine particles and having a small average diameter, for example, most of the particles fall in the range of 20 to 80μ , can be produced and supplied to the reaction system thereby to improve the fluidized state and contacting efficiency.

75 While the most suitable particle size distribution varies with the scale and system of the reaction apparatus, any requirements can be met by application of the method of the present invention.

80 The present invention will be further explained by reference to the following examples and comparison examples wherein, unless otherwise indicated, all parts, percentages and ratios are by weight.

Example 1

A catalyst for fluidized bed use and 120 having the empirical formula;



85 was produced as follows:

(I) 5.65 Kg of antimony trioxide powder was weighed out.

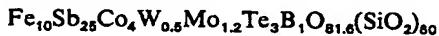
(II) 0.865 Kg of electrolytic iron powder was weighed out. A mixture of 6.25 l of nitric

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acid having a specific gravity of 1.38 and 7.75 l of water was heated to about 80°C, in which the iron powder was dissolved by gradually adding the iron powder thereto.		and 50% (Example 7), which was then homogenized. This slurry was spray-dried using a spray drying apparatus and at the same time, those fine particles of not more than 20 μ were classified and separated. The thus obtained particles were calcined under the same conditions as in Example 1.	65
5 (III) 13.9 Kg of a silica sol containing 20% by weight of SiO_2 was weighed out.			70
(I), (II), and (III) were mixed and the pH of the resulting mixture was adjusted to 2 by gradually adding aqueous ammonia of a concentration of 15% by weight while stirring well. The thus obtained slurry was heated for 2 hours at 100°C while stirring well.		Example 8 A catalyst for fluidized bed use and having the empirical formula:	
10 This slurry was then spray-dried using a rotary disc type spray drying apparatus and at this time fine particles of not more than 20 μ were caught by controlling the cyclone. These particles were wet-pulverized using a ball mill to control the diameter thereof to not more than 20 μ .		$\text{Fe}_{10}\text{Sb}_{25}\text{O}_{65}(\text{SiO}_2)_{30}$	75
15 This pulverised product was added to a slurry, which had been prepared by the same method as described above and which had been subjected to heating processing, in an amount of 5%, calculated as the oxides of completed catalyst, to which water was then added. The resulting mixture was homogenized. This slurry was spray-dried by the use of the above described spray drying apparatus, and at the same time those fine particles of not larger than 20 μ in diameter were classified and separated. The thus obtained particles were calcined for 2 hours at 200°C, for 2 hours at 400°C and further for 3 hours at 850°C.		A slurry prepared by the same method as described in Example 1 was spray-dried and at the same time, those particles of not more than 20 μ were classified and combined together. Pure water was added so that the amount of the above particles calculated as the oxides of the completed catalyst, was 20%, and the resulting mixture was heated to 100°C and allowed to stand for 30 minutes. After homogenization, the slurry was spray-dried and those fine particles of not more than 20 μ were classified and separated in the same manner as described above. The thus obtained particles were calcined under the same conditions as in Example 1.	80
20 Catalists for fluidized bed use and having the empirical formula: $\text{Fe}_{10}\text{Sb}_{25}\text{O}_{65}(\text{SiO}_2)_{30}$ were produced in the same manner as described in Example 1 except that the amount of the fine particle to be added to the slurry subjected to the heating processing was changed to 10% (Example 2), 15% (Example 3), 50% (Example 4) or 70% (Example 5), all calculated as the oxides of the completed catalyst.		Comparison Example 1 A catalyst for fluidized bed use and having the empirical formula: $\text{Fe}_{10}\text{Sb}_{25}\text{O}_{65}(\text{SiO}_2)_{30}$ was prepared as follows:	85
25 (I) 5.65 Kg of antimony trioxide powder was weighed out.		(I) 5.65 Kg of electrolytic iron powder was weighed out.	90
30 (II) 0.865 Kg of electrolytic iron powder was weighed out. A mixture of 6.25 l of nitric acid having a specific gravity of 1.38 and 7.75 l of water was heated to about 80°C, to which the above iron powder was gradually added to completely dissolve the iron therein.		(II) 0.865 Kg of electrolytic iron powder was weighed out. A mixture of 6.25 l of nitric acid having a specific gravity of 1.38 and 7.75 l of water was heated to about 80°C, to which the above iron powder was gradually added to completely dissolve the iron therein.	95
35 (III) 13.9 Kg of a silica sol containing 20% by weight of SiO_2 was weighed out.		(III) 13.9 Kg of a silica sol containing 20% by weight of SiO_2 was weighed out.	100
40 (I), (II), and (III) were mixed, and the pH of the mixture was adjusted to 2 by gradually adding aqueous ammonia of a concentration of 15% by weight while stirring well. The thus obtained slurry was heated for 2 hours at 100°C while stirring well.		This slurry was then spray-dried by using a rotary disc type spray drying apparatus. The thus obtained particles were calcined at 200°C for 2 hours, at 400°C for 2 hours and further at 850°C for 3 hours.	105
45 This pulverized product was added to a slurry, which had been produced in the same manner as in Example 1 and subjected to heating processing, in such a manner that the amount, calculated as the oxide of the completed catalyst, was 15% (Example 6)		Comparison Examples 2 to 5 Catalysts for fluidized bed use and having the empirical formula: $\text{Fe}_{10}\text{Sb}_{25}\text{O}_{65}(\text{SiO}_2)_{30}$ were produced as follows:	110
50 Catalists for fluidized bed use and having the empirical formula: $\text{Fe}_{10}\text{Sb}_{25}\text{O}_{65}(\text{SiO}_2)_{30}$ were produced as follows:		The finally calcined catalyst obtained by	115
55 A slurry prepared by the same method as described in Example 1 was subjected to a spray drying operation. At this time, cakes remaining in the spray drying apparatus, i.e., spray-dried masses, were removed from the apparatus and these cakes were wet-pulverized in a ball mill to reduce the particle diameter to not more than 10 μ .			120
60 This pulverized product was added to a slurry, which had been produced in the same manner as in Example 1 and subjected to heating processing, in such a manner that the amount, calculated as the oxide of the completed catalyst, was 15% (Example 6)			

the method of Comparison Example 1 was wet-pulverized in a ball mill to reduce the particle diameter to not more than 10 μ . This pulverized product was added to a slurry, which had been prepared by the same method as in Comparison Example 1 and subjected to the heating processing, so that the amount calculated as the oxides of the catalyst was 10% (Comparison Example 2), 15% (Comparison Example 3), 50% (Comparison Example 4) or 60% (Comparison Example 5). Water was then added thereto and the resulting mixture was homogenized. The thus obtained slurry was spray-dried and the particles so obtained were calcined under the same conditions as in Comparison Example 1.

Example 9
A catalyst for fluidized bed use and having the empirical formula:



was produced as follows:

(I) 2.92 Kg of antimony trioxide powder was weighed out.

(II) 0.447 Kg of electrolytic iron was weighed out. A mixture of 3.2 l of nitric acid (specific gravity 1.38) and 2 l of water was heated. To this mixture was added the iron powder little by little to dissolve the iron therein. 0.932 Kg of cobalt nitrate was added thereto.

(III) 105 g of ammonium tungstate and 170 g of ammonium molybdate were dissolved in 920 ml of water. In addition, 525 g of telluric acid was added and dissolved therein.

(IV) 9.61 Kg of a silica sol containing 30% by weight of SiO_2 was weighed out, in which 49 g of boric acid was dissolved.

To (IV) were added (III), (II), and (I) in this order. The pH of the resulting mixture was adjusted to 2 by adding 15% aqueous ammonia while stirring well. The mixture was heated at 100°C for 8 hours with good stirring. This slurry was spray-dried with a rotary disc type spray drying apparatus. From the spherical particles so obtained were separated those particles having a diameter of not more than 20 μ and not less than 80 μ by the use of a classification apparatus. The particles of not more than 20 μ and not less than 80 μ were combined together and wet-pulverized. This pulverized product was added to a slurry, which had been prepared by the same method as described above and subjected to the heating processing, so that the amount calculated as the oxides of the catalyst was 20% and the resulting mixture was then stirred well. The slurry was spray-dried by the use of the above spray drying apparatus. From the thus obtained spherical particles

were separated those particles having a diameter of not more than 20 μ and not less than 80 μ by the use of a classification apparatus in the same manner as described above.

The thus obtained particles were calcined at 250°C for 8 hours, at 400°C for 16 hours and finally at 700°C for 4 hours.

Comparison Example 6
A catalyst for fluidized bed use and having the empirical formula:



was produced as follows:

A slurry subjected to the heating processing was prepared by the same method as in Example 9, and this slurry was spray-dried by the use of a rotary disc type spray drying apparatus. The spherical particles so obtained were calcined under the same conditions as in Example 9.

Example 10
A catalyst for fluidized bed use and having the empirical formula:



was produced as follows:

(I) Antimony pentachloride was hydrolyzed with aqueous ammonia and the resulting product was weighed out in an amount of 2.59 Kg calculated as Sb_2O_5 .

(II) 0.358 Kg of electrolytic iron was weighed out. 3 l of nitric acid having a specific gravity of 1.38 was mixed with 4 l of water, which was then heated to about 80°C. In this mixture was dissolved completely the iron powder by gradually adding the iron thereto.

(III) 41.8 g of ammonium tungstate was weighed out and dissolved in 1.5 l of water.

(IV) 147 g of telluric acid was weighed out and dissolved in 1 l of water.

(V) 3.84 Kg of a silica sol containing 30% by weight of SiO_2 was weighed out.

(I), (II), (III), (IV) and (V) were mixed and the pH of the resulting mixture was adjusted to 1 by gradually adding aqueous ammonia of a concentration of 15% by weight while stirring well.

The thus obtained slurry was heated at 100°C for 4 hours while stirring.

This slurry was then spray-dried by the use of a rotary disc type spray-drying apparatus. From the spherical particles so obtained were separated those particles of not more than 25 μ and not less than 80 μ by the use of a classification apparatus. The particles of not more than 20 μ and not less than 80 μ were wet-pulverized in a vibration mill. This pulverized product was added to a slurry, which had been produced by the

8	1,553,801	8
5	same method as described above and subjected to the heating processing, so that the amount calculated as the oxides of the completed catalyst was 10%. The mixture so obtained was stirred well. This slurry was spray-dried by the use of the above described spray drying apparatus. From the spherical particles so obtained were separated those particles of not more than 25 μ and not less than 80 μ by the use of a classification apparatus in the same manner as described above.	55
10	The thus obtained particles were calcined at 200°C for 4 hours, at 400°C for 4 hours and finally at 830°C for 4 hours.	60
15	Comparison Example 7 A catalyst for fluidized bed use and having the empirical formula:	65
	$Fe_{10}Sb_{25}W_{0.25}Te_{1.0}O_{67.75}SiO_2$	70
20	was produced as follows: A slurry was prepared by the same method as in Example 10 and spray-dried by the use of a rotary disc type spray drying apparatus. The spherical particles obtained were calcined under the same conditions as in Example 10.	75
25	Example 11 A catalyst for fluidized bed use and having the empirical formula:	80
30	$U_{10}Sb_{40}O_{106.7}(SiO_2)_{50}$	85
	was produced as follows: (I) 4.79 Kg of antimony pentachloride was weight out. A lump of ice was floated in 20 l of water, into which antimony pentachloride was gradually poured. Then 28% aqueous ammonia was gradually added thereto to adjust the pH thereof to 8. The precipitate formed was filtered and washed three times with 3 l of water. (II) 2.0 Kg of uranyl nitrate	90
35	$(UO_2(NO_3)_2 \cdot 6H_2O)$	95
40	was weighed out and dissolved in 5 l of water	100
	C conversion (III) 6 Kg of a silica sol containing 20% by weight of SiO_2 was weighed out.	105
45	(I), (II) and (III) were mixed, and the pH of the resulting mixture was adjusted to 2.0 by gradually adding 15 wt% aqueous ammonia while stirring well.	110
50	The thus obtained slurry was heated at 100°C for 5 hours while stirring well. This slurry was spray-dried in a conventional manner by the use of a rotary disc type spray drying apparatus. From the	115
	spherical particles obtained were separated those particles of not more than 20 μ and not less than 80 μ by the use of a classification apparatus. The particles of not more than 20 μ and not less than 80 μ were combined together and wet-pulverized in a vibration mill so that the particle diameter was not more than 10 μ . This pulverized product was added to a slurry, which had been prepared by the same method as described above and subjected to the heating processing, so that the amount calculated as the oxide of the completed catalyst was 18%. The resulting mixture was stirred well. Then the slurry was spray-dried with the above described spray drying apparatus. From the spherical particles so obtained were separated those particles of not more than 20 μ and not less than 80 μ in the same manner as described above by the use of a classification apparatus.	55
	The thus obtained particles were calcined at 200°C for 4 hours, at 400°C for 4 hours and finally at 800°C for 4 hours.	60
	Comparison Example 8 A catalyst for fluidized bed use and having the empirical formula: $U_{10}Sb_{40}O_{106.7}(SiO_2)_{50}$ was produced as follows: A slurry was prepared by the same method as used in Example 11 and subjected to the heating processing. This slurry was spray-dried by the use of a rotary disc type spray drying apparatus. The spherical particles obtained were calcined under the same conditions as employed in Example II.	65
	Example 12 A catalyst for fluidized bed use and having the empirical formula:	70
	$Fe_{10}Sb_{20}Mo_{0.5}W_{0.2}Te_{1.5}Cu_{1.5}Ni_3O_{64.1}(SiO_2)_{50}$	75
	was produced as follows: The same method as in Example 1 was employed except that ammonium paramolybdate, ammonium tungstate, telluric acid, copper nitrate and nickel nitrate were used as the starting materials for Mo, W, Te, Cu and Ni, respectively. These materials were added to the slurry prior to the adjustment of pH to produce a heat-processed slurry.	80
	This slurry was then spray-dried in a conventional manner by the use of a rotary disc type spray drying apparatus, and at this time, those particles of not more than 20 μ were classified and caught by controlling a cyclone classifier. These particles were wet-pulverized by the use of a ball mill to reduce the diameter to not more than 15 μ .	85
	This pulverized products was added to a slurry, which had been produced by the	90

- same method as described above and subjected to the heating processing, so that the amount was 15% calculated as the oxide of the completed catalyst, and the resulting mixture was stirred well. The mixture was then spray-dried by the use of the above spray drying apparatus and those particles of not more than 20 μ were separated by controlling the cyclone.
- 10 The spherical particles so obtained were calcined under the same conditions as in Example 1.

- Example 13**
A catalyst for fluidized bed use and having the empirical formula:



was produced by the same method as in Example 12. In this case, however, ammonium metavandate and zinc nitrate were used as the starting materials for V and Zn, respectively. Classification, pulverization, amount of pulverized product to be added, and calcination of the spherical particles obtained were effected under the same conditions as in Example 12.

- Example 14**
A catalyst for fluidized bed use and having the empirical formula:



30 was produced by the same method as in Example 12. In this case, however, magnesium nitrate was used as the starting material for Mg. Classification, pulverization, amount of the pulverized product to be added, and calcination of the spherical particles obtained were conducted under the same conditions as in Example 12.

- Test Methods and Test Results of Catalysts**
40 The catalysts obtained in the above examples and comparison examples were tested.

- (a) **Catalyst Attrition Resistance Test**
This test was conducted in accordance with the method described in "Test Methods for Synthetic Cracking Catalysts" 6/31—4m—1/57, published by American Cynamid Co., and known in the art as a test method for fluid catalytic cracking catalysts, the so-called FCC-catalysts.
- 45 The test was conducted on catalyst particles ranging from 44 to 88 microns in diameter
- The R-value with respect to attrition loss (percent) given in Table 1 were calculated on the basis of the following relationship.

$$R = \frac{B}{C-A} \times 100$$

wherein A represents the weight in grams of catalytic lost by attrition continued for a period of time from 0 to 5 hours; B represents the weight in grams of catalyst lost by attrition continued for a period of time of from 5 to 20 hours; and C represents the weight in grams of catalyst tested by the present test (c = 50 in the tests here conducted). A smaller value indicates greater strength.

(b) **Catalytic Activity Test**

A catalyst was charged to a reactor in which the inner diameter of a fluidized catalyst area was 2 inches and baffle plates were provided therein in such a manner that a predetermined contact time was obtained.

As starting materials, propylene, ammonia and air were introduced into the above reactor in a proportion of 1:1.2:11 (molar ratio) so as to provide a linear velocity of 13 cm/sec.

Gaseous products were gas-chromatographed for quantitative analysis.

With regard to the results obtained, catalyst attrition resistance test results are shown in Table 1 and catalyst activity test results are shown in Table 2. The particle size distribution of the catalysts of the examples and comparison examples are shown in Table 3.

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TABLE I
Comparison
Invention

Catalyst	Proportion of Pulverized Product Present (wt.%)	Attrition Loss			Proportion of Pulverized Product Present (wt.%)	Attrition Loss (wt.%)
		Catalyst	Attrition Loss (wt.%)	Comparison		
Ex. 1	5		2.0	Com. Ex. 1	0	2.3
Ex. 2	10		1.8	Com. Ex. 2	10	2.4
Ex. 3	15		1.9	Com. Ex. 3	15	3.1
Ex. 4	50		2.0	Com. Ex. 4	90	4.3
Ex. 5	70		1.9	Com. Ex. 5	60	18
Ex. 6	15		1.7			
Ex. 7	50		2.0			
Ex. 8	100		2.2			
Ex. 9	20		1.9	Com. Ex. 6	0	2.0
Ex. 10	10		1.0	Com. Ex. 7	0	1.3
Ex. 11	18		1.2	Com. Ex. 8	0	1.3
Ex. 12	15		1.6			
Ex. 13	15		1.0			
Ex. 14	15		1.5			

TABLE 2

Catalyst	Reaction Temperature (°C)	Contact Time (sec)	Yield of Acrylonitrile (%)
Ex. 6	460	6	66
Ex. 8	460	6	67
Com. Ex. 1	460	6	65
Ex. 9	430	4	82
Com. Ex. 6	430	4	82
Ex. 12	430	4	84

Note :

$$(1) \text{ Yield of Acrylonitrile (\%)} = \frac{\text{Moles of Acrylonitrile Produced}}{\text{Moles of Propylene Fed}} \times 100$$

(2) In the catalyst column, Ex. 1, for example, means that the catalyst produced in Example 1 was tested.

TABLE 3

Particle Size Distribution (wt %)

Catalyst	Less than 20 μ	Less than 44 μ	Greater than 88 μ	Average Size (50% diameter) (μ)
Ex. 1	1	38	8	51
.. 2	0	32	11	53
.. 3	2	39	9	50
.. 4	0	42	7	48
.. 5	0	37	13	52
.. 6	0	35	11	52
.. 7	0	36	15	54
.. 8	0	37	12	52
.. 9	1	47	2	49
.. 10	0	37	2	53
.. 11	0	45	0	47
.. 12	2	35	10	46
.. 13	1	38	8	50
.. 14	1	36	12	50
Com. Ex. 1	9	48	10	46
.. 2	8	46	11	48
.. 3	10	49	9	45
.. 4	12	50	7	44
.. 5	11	47	8	46
.. 6	11	51	7	43
.. 7	10	48	8	46
.. 8	15	48	10	45

Summary of Test Results

The results in Table 1 indicate that the catalysts prepared in the Examples had good strength irrespective of the proportion of the pulverized product incorporated therein.

The results in Table 2 indicate that the catalysts prepared in the Examples did not adversely influence the reaction even

though the pulverized product of the spray-dried product was incorporated therein.

With regard to the loss of the catalyst, the catalyst activity test results indicate that there was no loss in catalyst with the catalyst of the Examples wherein the catalysts of the Comparison Examples, catalyst was lost during the reaction.

WHAT WE CLAIM IS:—

1. A process for producing an attrition-resistant, antimony oxide-containing fluidized bed catalyst having a controlled particle size distribution, the process comprising:
 5 (a) preparing a slurry containing at least one pentavalent antimony compound, one or more polyvalent metal or metalloid compounds and a silica sol as essential components;
 10 (b) adjusting the pH of the above slurry to not more than 7 and heating the slurry at a temperature of from 40°C to 150°C for at least 20 minutes while keeping the mixture in a slurried state to form a slurry containing pentavalent antimony;
 15 (c) spray drying the thus obtained slurry to form substantially spherical particles;
 20 (d) separating extremely fine particles and/or coarse particles unsuitable for practical use from the above obtained spherical particles and returning these separated particles to the slurry prior to the spray drying in step (c) either untreated or after pulverization thereof; and
 25 (e) calcining the particles not containing the extremely fine particles and/or coarse particles at a temperature of from 400° to 1100°C.
 30 2. A process according to Claim 1, wherein said at least one pentavalent antimony compound is selected from antimony pentoxide, antimonic acid, antimony pentachloride, antimony pentoxide sol and the oxidized product of antimony trioxide with hydrogen peroxide or potassium permanganate.
 35 3. A process according to Claim 1 or Claim 2, wherein said one or more polyvalent metal or metalloid compounds is or are selected from compounds of iron, cobalt, nickel, tin, uranium, chromium, copper, manganese, titanium, vanadium, molybdenum, tungsten, tellurium, bismuth, thorium, cerium, magnesium, zinc, aluminium and zirconium.
 40 4. A process according to any preceding claim, wherein the atomic ratio of the metal or metalloid in the polyvalent metal or metalloid compound to the antimony in the antimony compound ranges from 1:10 to 5:1.
 45 5. A process according to any preceding claim, wherein in the spray-drying of step (c), the temperature of the hot air ranges from 200°C to 500°C at an inlet portion of the spray-drying apparatus, and ranges from 100°C to 300°C at an outlet portion of the spray-drying apparatus.
 50 6. A process according to any preceding claim, wherein those particles having a diameter of not more than 20 μ and of not less than 200 μ are separated from the spherical particles obtained in the spray-drying of step (c).
 55 7. A process according to any one of Claims 1 to 5, wherein those particles having a diameter of not less than 80 μ are separated from the spherical particles obtained in the spray drying of step (c).
 60 8. A process according to Claim 6, wherein the particles separated are pulverized to reduce the diameter thereof to not more than 10 μ.
 65 9. A process according to Claim 1, wherein the spherical particles obtained by the spray drying of step (c), from which the extremely fine particles and/or coarse particles have been separated, comprise those particles of a diameter of not more than 20 μ constituting not more than 5% by weight of the total weight of the particles and those particles of a diameter of not less than 200 μ constituting not more than 15% by weight of the total weight of the particles.
 70 10. A process for producing an attrition resistant antimony oxide containing fluidized bed catalyst having a controlled particle size distribution, the process comprising:
 75 (a) preparing a slurry containing a trivalent antimony compound, one or more polyvalent metal or metalloid compounds, a silica sol, ferric ions and nitrate ions as essential components;
 80 (b) adjusting the pH of the slurry to not more than 7 and then heating the slurry at a temperature of from 40°C to 150°C for at least 20 minutes while keeping the mixture in a slurried state to form a slurry containing pentavalent antimony;
 85 (c) spray-drying the slurry so obtained to form substantially spherical particles;
 90 (d) separating those extremely fine particles and/or coarse particles unsuitable for practical use from the particles obtained and returning the particles separated to the slurry prior to the spray drying of step (c) either untreated or after pulverization thereof; and
 95 (e) calcining the particles not containing the extremely fine particles and/or coarse particles at a temperature of from 400° to 1100°C.
 100 11. A process according to Claim 10, wherein said at least one trivalent antimony compound is selected from antimony trioxide, antimony trichloride, the nitric acid oxidized product of metallic antimony, and the hydrolysis product of antimony trichloride.
 105 12. A process according to Claim 10 or Claim 11, wherein said at least one polyvalent metal or metalloid compound is or are selected from compounds of iron, cobalt, nickel, tin, uranium, chromium, copper, manganese, titanium, vanadium, molybdenum, tungsten, tellurium, bismuth, thorium, cerium, magnesium, zinc, 110
 115 120
 120 125
 125 130

- aluminium and zirconium.
13. A process according to Claim 10, 11 or 12, wherein the atomic ratio of the metal or metalloid in the polyvalent metal or metalloid compound to the antimony in the antimony compound is from 1:10 to 5:1.
- 5 14. A process according to any one of Claims 10 to 13, wherein for the spray drying of step (c), the temperature of the hot air ranges from 200°C to 500°C at an inlet portion of the spray-drying apparatus, and ranges from 100°C to 300°C at an outlet portion of the spray-drying apparatus.
- 10 15. A process according to any one of Claims 10 to 14, wherein those particles of a diameter less than 20 μ and/or those particles of a diameter more than 200 μ are separated from the spherical particles obtained by the spray drying of step (c).
- 15 16. A process according to any one of Claims 10 to 14 wherein the particles of a diameter more than 80 μ are separated from the spherical particles obtained by the spray drying of step (c).
- 20 17. A process according to Claim 15, wherein the particles separated are pulverized to reduce the diameter thereof to not more than 10 μ .
- 25 18. A process according to any one of Claims 10 to 17 wherein the spherical particles obtained by the spray drying of step (c), from which the extremely fine particles and/or coarse particles have been separated, comprise those particles of a diameter of not more than 20 μ constituting not more than 5% by weight of the total weight of the particles and those particles of a diameter not less than 200 μ constituting not more than 15% by weight of the total weight of the particles.
- 30 19. A process for producing an attrition-resistant, antimony oxide-containing fluidised bed catalyst, substantially as hereinbefore described in any one of Examples 1 to 14.
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